

Negative magnetocaloric effect from highly sensitive metamagnetism in $\text{CoMnSi}_{1-x}\text{Ge}_x$

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We report a novel negative magnetocaloric effect in $\text{CoMnSi}_{1-x}\text{Ge}_x$ arising from a metamagnetic magnetoelastic transition. The effect is of relevance to magnetic refrigeration over a wide range of temperature, including room temperature. In addition we report a very high shift in the metamagnetic transition temperature with applied magnetic field. This is driven by competition between antiferromagnetic and ferromagnetic order which can be readily tuned by applied pressure and compositional changes.

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Whilst the magnetocaloric effect (MCE) has been known since 1881 [1], it has only recently been thought of as providing a potential alternative to conventional gas compression refrigeration in the room temperature range. The conventional, positive, MCE—where a material heats when a magnetic field is applied adiabatically—has historically been used to achieve mK temperatures for scientific research by demagnetisation of paramagnetic salts. However, the effect is largest around sharp magnetic transitions, and recent work has demonstrated giant MCEs near first order magnetic transitions that, by varying material composition and/or applied magnetic field, occur over a wide range of temperatures extending above room temperature [2, 3].

There has already been significant progress in the design of prototype magnetic refrigerators [4], fuelled by the prediction that such devices could impact on carbon emissions as they are potentially 40% more efficient than a conventional refrigerator [5]. However, initial excitement arising from such developments has been tempered by two factors: the size of the magnetic fields required and the cost of the magnetocaloric refrigerants. Ideally, permanent magnets (of strength below 2 Tesla) should be used. In contrast, many prototype refrigerators have used high fields generated by superconducting coils. On the second point, high purity gadolinium, on which several proposed magnetocaloric alloys are based, has a cost of the order of \$500/kg. Less expensive alternative refrigerants suffer from other problems: martensitic Heusler alloys such as $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ and $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Sn}$ have a large magnetic hysteresis [6, 7]; $\text{MnFeP}_{1-x}\text{As}_x$ [3] and MnAs-based materials [8] contain toxic As. $\text{Fe}_{0.49}\text{Rh}_{0.51}$ is both expensive and loses its negative MCE upon multiple cycling of the applied field [9].

Almost all room temperature magnetocalorics exhibit a positive MCE associated with a Curie transition. Only the metamagnets FeRh and $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Sn}$ have exhibited a significant negative magnetocaloric effect, where the material cools when a field is applied. The lack of study of metamagnetic transitions by the mag-

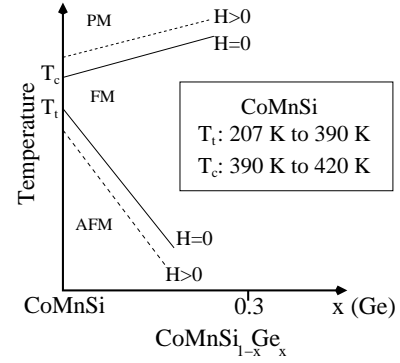


FIG. 1: Schematic magnetic phase diagram of $\text{CoMnSi}_{1-x}\text{Ge}_x$, after Nizioł et al. [11]. Both the temperature of the transition between paramagnetic (PM) and ferromagnetic (FM) states, T_c and that between the FM and antiferromagnetic (AFM) states, T_t shift with Ge content and applied magnetic field, H as shown. Exact temperatures are not shown due to the variability in literature data (see inset). Hydrostatic pressure also reduces T_t (see text).

netocaloric community is surprising given that they are more likely to be first order than their ferromagnetic cousins. In this Letter we study the pseudoternary metamagnet $\text{CoMnSi}_{1-x}\text{Ge}_x$, a novel room temperature negative magnetocaloric material system which addresses the issues of cost, hysteresis and toxicity outlined above. In particular we draw attention to the rapid variation of its metamagnetic transition temperature, T_t with magnetic field (large $|\partial T_t / \partial H|$). This highly desirable property usually brings about a large adiabatic temperature change in a magnetocaloric material when it is exposed to a rapid change in applied magnetic field over a wide range of working temperatures. We will show in particular that CoMnSi exhibits an MCE over a wide range of temperatures, but this MCE is limited by such a high $|\partial T_t / \partial H|$. We will point to ways in which CoMnSi might be optimised from this point of view.

The various magnetic phases of the $\text{CoMnSi}_{1-x}\text{Ge}_x$ material system were examined by Nizioł and coworkers

ers in the 1970s and 1980s [10, 11]. This paper will focus on the range $x < 0.1$. CoMnSi is orthorhombic, with space group $Pnma$ and exhibits competition between helical non-collinear antiferromagnetic order and ferromagnetic order. It is antiferromagnetic at low temperatures and shows a sample-dependent first order metamagnetic transition to a ferromagnetic state at a transition temperature T_t of between 207 K and 360 K [12]. The ferromagnetic state has a second order T_c which in much of the literature is at about 390 K [11]. A schematic phase diagram of the orthorhombic phase of CoMnSi $_{1-x}$ Ge $_x$ for $x < 0.3$ is summarised in Figure 1.

We concentrate here on the first order metamagnetic transition at T_t in CoMnSi $_{1-x}$ Ge $_x$. We note that other authors have found a wide variation in the zero-field value of T_t . Medvedeva quotes a value of 260 K in a 1 Tesla field [13] from samples made by melting elemental Co, Mn and a 1% excess of Si together in a high frequency furnace under an argon atmosphere. Early work by Bińczycka *et al.* found values as low as 207 K in samples grown by melting elemental Co, Mn and Si, followed by annealing at 1273 K and rapid quenching [14]. The latter results were later attributed to a lack of sample homogeneity, and a higher T_t was obtained by a change in growth method [12]. Specifically, the change involved melting binary CoSi and elemental Mn, followed by annealing at temperatures between 1000 K and 1200 K. We note here that the choice of annealing routine (hold temperature and rate of cooling) was also observed to have an effect on the magnetic properties of CoMnSi as early as 1973 in the work of Johnson and Frederick [15], and was cited as the main cause for the sample dependent magnetic behaviour in the work of Medvedeva [13].

Thus, the precise magnetism of CoMnSi has been found to be extremely sample dependent. We suggest that this may be because the magnetism of this material is highly sensitive to the separation of manganese atoms, on which most of the magnetic moment is to be found [12]. Both small amounts of Ge substitution on the Si site and the application of hydrostatic pressure have been shown to cause a rapid decrease in T_t . The rate of change of T_t with pressure is very high: dT_t/dp is between -60 K/GPa [13] and -100 K/GPa [16]. Previous crystallographic work shows that there is a volume contraction associated with the transition from the low temperature antiferromagnetic state to the high temperature ferromagnetic state [12]. This would explain why the application of hydrostatic pressure stabilises the ferromagnetic phase, reducing T_t [13, 16]. Although Ge substitution expands the lattice relative to stoichiometric CoMnSi, perhaps the reduction of T_t in that instance is driven by a change in the thermal expansion properties of the material. (For example, if the critical atomic separation for a change in the exchange interaction is reached at a lower temperature—see later.) There is also the possibility of the observed variability in sample behaviour

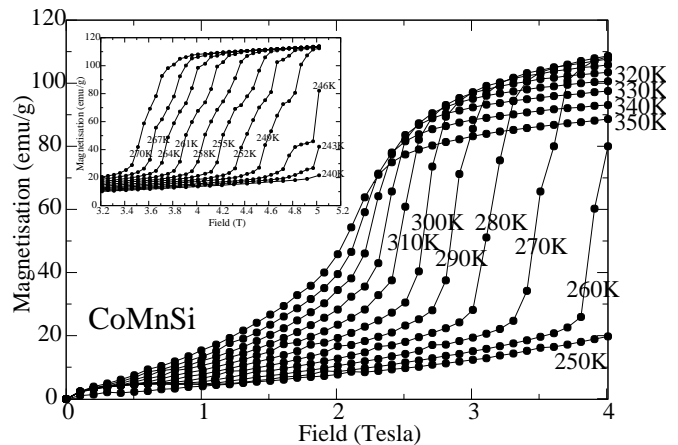


FIG. 2: Magnetisation versus field for CoMnSi, at 10 K intervals in temperature, between 250 K and 350 K. The inset shows the same measurement between 240 K and 270 K in 3 K intervals. In this temperature range, the metamagnetic field is in the range 3.4 T to 5 T and the metamagnetic transition appears to split in two.

being controlled by atomic disorder, as yet unquantified.

In small fields, the metamagnetic transition at T_t is probably to a fan spin state of small net moment. Previous literature indicates that fields of around 2 Tesla are required to observe a transition at T_t in CoMnSi at 280 K [10] to a state approaching a large magnetisation of 100 emu/g. Here, we seek to obtain a unified picture of the effects of substitution, pressure and magnetic field on the tunability of the metamagnetic transition in a set of identically fabricated samples of CoMnSi $_{1-x}$ Ge $_x$. The variability and possible tunability of T_t in CoMnSi makes this material an interesting candidate magnetic refrigerant if we can readily alter the region of temperature where the isothermal entropy change, ΔS is maximal and where the largest magnetocaloric effect is found.

Samples were prepared by induction melting pieces of elemental Mn (99.99%), Co (99.95%), Si and Ge (both 99.9999%) in 1 bar of argon. Weight losses were 0.3% to 0.5%. All samples were annealed in evacuated silica ampoules at 1223 K for 60 hours, and slowly cooled to room temperature at a rate of 0.2 K per minute. X-ray diffraction of powdered samples showed only an orthorhombic ($Pnma$) phase. Scanning electron microscopy images of the materials showed a lack of significant contrast, which, if present, would be indicative of compositional variations. These two observations suggest the absence of a second phase. Rietveld refinement of lattice parameters and atomic coordinates was also performed. Magnetic measurements were performed in a vibrating sample magnetometer (maximum field 1.8 T) and a SQUID (maximum field 5 T).

From low field magnetisation measurements, we found $T_t \sim 390$ K and $T_c \sim 420$ K for CoMnSi; the highest values yet recorded for this material. In Figure 2 we show

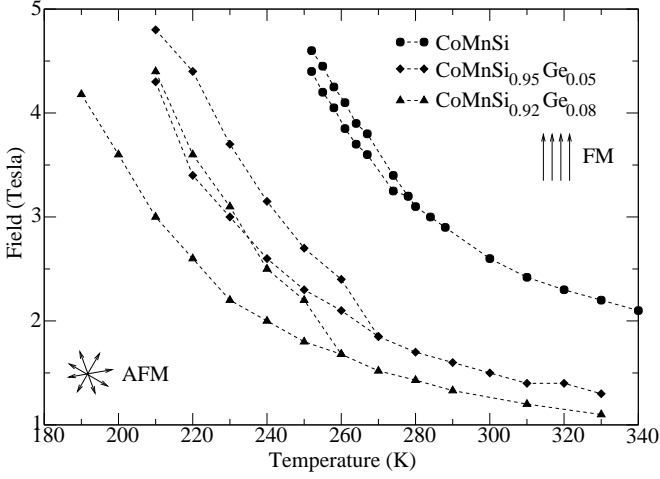


FIG. 3: Variation of the metamagnetic transition temperature T_t with applied field, for $\text{CoMnSi}_{1-x}\text{Ge}_x$ ($x=0, 0.05$ and 0.08). In each case, the metamagnetic transition splits into two transitions at the highest fields.

the isothermal magnetisation vs applied field for CoMnSi at temperatures between 250 K and 350 K. Data at each temperature was taken in increasing fields directly after zero field cooling from 350 K. The first order metamagnetic transition is very sensitive to applied field: it shifts by 100 K in the range 2 T to 4 T. Just as T_t is higher than hitherto measured, so the metamagnetic transition fields at a given temperature are larger than previously found. Corresponding magnetisation curves were obtained for $\text{CoMnSi}_{1-x}\text{Ge}_x$ with $x = 0.05$ or 0.08 . These lead to the magnetic phase diagram shown in Fig. 3. In all cases, the metamagnetic field was taken as the point(s) of inflexion in the $M(H)$ curve. In all three compounds the transition seems to split in two in the highest applied fields. This is illustrated for CoMnSi in the inset to Figure 2, and the splitting becomes more pronounced as the level of Ge substitution is increased. At this stage we cannot establish whether the splitting of the metamagnetic transition is due to a lack of homogeneity or is a consequence of a high field transition to an intermediate, canted ferromagnetic state, as predicted for helical anti-ferromagnets by Nagamiya [17]. We note that previous authors associated a canted state with a much smaller magnetic crossover feature at lower fields [10].

We use a Maxwell relation to obtain the isothermal change in total entropy from the isothermal $M(H)$ curves:

$$\Delta S_{\text{total}}(T, \Delta H) = \int_0^{H_{\text{final}}} \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (1)$$

This still holds true in the first order scenario if we choose to ignore magnetic and thermal hysteresis for the moment. It is a fair approximation as the measured thermal hysteresis in CoMnSi is only 3 K at 3 Tesla, corresponding to a small shift in the metamagnetic transition field

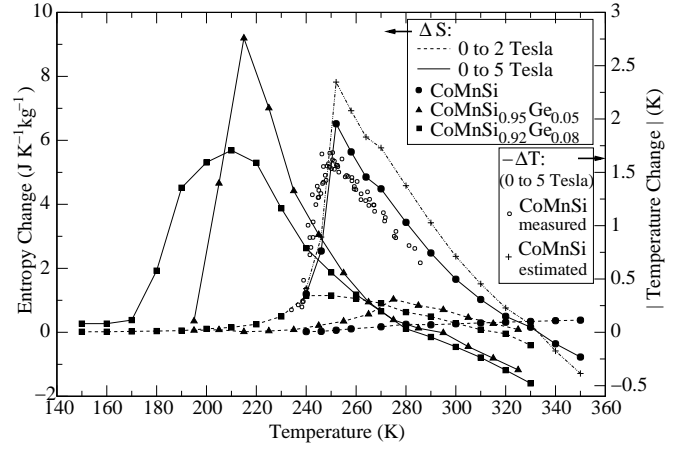


FIG. 4: The isothermal entropy change of $\text{CoMnSi}_{1-x}\text{Ge}_x$ ($x=0, 0.05$ and 0.08), on changing the applied field from zero to either 2 Tesla or 5 Tesla. Also shown is the magnitude of the negative adiabatic temperature change, ΔT , of CoMnSi when the applied field is raised from zero to 5 Tesla, together with an estimate of ΔT using our ΔS data and Eq. 3.

of around 0.1 Tesla. From Equation 1, and the $M(H, T)$ data, entropy change curves for each of the three compounds were obtained and are shown in Figure 4. In a field change of 5 Tesla, all three compounds display a large, broad, positive isothermal entropy change associated with T_t and the onset of a negative change associated with T_c . For a large entropy change associated with the metamagnetic transition to be observed, T_t must be far removed from the Curie temperature. This necessitates fields in excess of ~ 2 Tesla. Ge substitution reduces the fields and temperatures required for the metamagnetic transition relative to those in CoMnSi , as expected. However, the transition is made less first order by substitution, so there is not a great increase in the size of ΔS for a given applied field. We henceforth focus on CoMnSi , for which there exists the greatest amount of literature data with which to make comparisons. The entropy change in CoMnSi is smaller than that in other metamagnets previously investigated (FeRh , Mn_3GaC) and this is consistent with another observation. The rate at which the metamagnetic transition temperature changes with applied field is very large—as high as -50 K/T in low fields (right hand side of Figure 3), compared to -8 K/T for FeRh [18] and -5 K/T for Mn_3GaC [19]. Such a large magnitude of $\partial T_t / \partial H$ (or, equivalently, small $\partial H_c / \partial T$) enables a wide range of working temperatures to be covered by a single material, although it also reduces the isothermal ΔS , as given by the Clausius Clapeyron equation for first order magnetic phase transitions:

$$\Delta S_{\text{total}}(T, \Delta H) = -\Delta M \left(\frac{\partial H_c}{\partial T} \right) = -\Delta M \left(\frac{\partial T_t}{\partial H} \right)^{-1}. \quad (2)$$

Here ΔM is the change in magnetisation at the transi-

tion, assumed to be independent of the strength of the applied field. Once fields in excess of 2 Tesla are applied to $\text{CoMnSi}_{1-x}\text{Ge}_x$, the metamagnetic transition becomes more first order and $\partial T_t/\partial H$ decreases in magnitude, both factors leading to a much enhanced isothermal entropy change. Nevertheless, the extraordinarily large $\partial T_t/\partial H$ of CoMnSi in fields below 2 Tesla has a profound effect on the adiabatic temperature change, ΔT :

$$\Delta T(T, \Delta H \equiv H) \sim -\frac{T}{C_H} \Delta S_{\text{total}}(T, \Delta H \equiv H) \quad (3)$$

where C_H is the field-dependent heat capacity in the region of the magnetic transition. We then see, by connection to Equation 2, that a very large $\partial T_t/\partial H$, as in the case of CoMnSi , severely reduces the adiabatic ΔT . We have also measured this adiabatic ΔT in a field change of zero to 5 Tesla over a temperature range of 230 K to 290 K, using a K-type thermocouple attached to a sample much larger than the dimensions of the thermocouple, all encased in teflon. Fields were generated in an 8 Tesla Oxford Instruments cryostat. As can be seen from the data in Figure 4, the resulting $\Delta T(T)$ curve peaks at nearly 2 K at ~ 250 K and is consistent with a crude estimate which may be obtained by using the 5 Tesla $\Delta S(T)$ curve and Eq. 3 with a fixed value of heat capacity, taken here to be 700 J/kg, the value we obtain at T_t in zero field measurements using a TA Instruments Q1000 DSC.

Our data, when compared with that from previous studies on CoMnSi , opens up the possibility of tuning the behaviour of the metamagnetic transition in this material, perhaps through heat treatment. We suggest here that the fact that our material has the highest recorded zero-field T_t and the highest H_c at a given temperature may be related to the observation that it has the largest measured lattice a parameter (5.868 Å) at room temperature. It is known that there is a reduction in the a parameter as the temperature is increased towards the metamagnetic transition [12]. Therefore, a high room temperature value of a might yield the observed high zero-field value of T_t if the metamagnetic transition occurs at a favoured lattice spacing, as suggested in the phenomenology of Kittel [20]. This is shown graphically in Figure 5 where extrapolations of measured lattice a parameter to the metamagnetic transition temperature yield approximately the same critical value of a . We include in this plot two of our CoMnSi samples; one slowly cooled after annealing (our usual heat treatment), and a second sample quenched instead of slowly cooled, which had a broad metamagnetic transition at around 300 K and a reduced room temperature lattice a parameter of 5.846 Å. The parameter leading to the differences between samples in the literature and in this study may be the annealing method. Annealing is made necessary in this material because of a structural phase transition from a hexagonal phase at around 1100 K encountered on cooling from the molten state during synthesis [11]. Documented an-

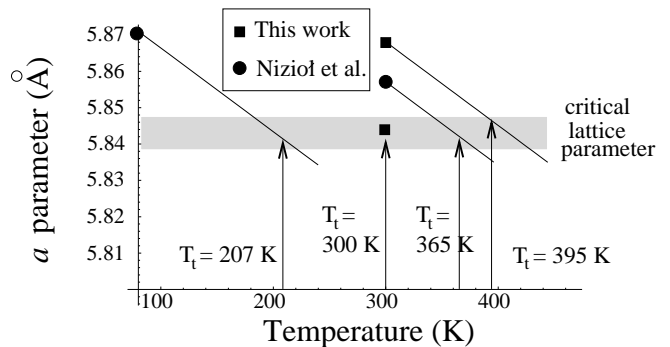


FIG. 5: The points show the measured a -axis parameter for samples of CoMnSi annealed in different ways [10, 12, 14]. Extrapolations of a to higher temperature, based on a fixed value of $da/dT = -2.3 \times 10^{-4} \text{ ÅK}^{-1}$ (extracted from Nizioł et al. [12]) are also shown. The experimentally observed metamagnetic transition temperatures (arrows) correspond approximately to the same critical value of a of about 5.84 Å.

nealing temperatures vary considerably, and there is incomplete information in the literature about the rates of cooling used. It may be possible that different hold temperatures and cooling rates freeze in different lattice strains, altering the separation of Mn atoms, and thereby the sensitive metamagnetic properties of CoMnSi .

We conclude that suitable systematic control of the magnetic exchange interactions and/or atomic order could adjust H_c , T_t and $|\partial T_t/\partial H|$ and thereby make CoMnSi a useful new negative magnetocaloric in relatively low magnetic fields. We have demonstrated that a very sensitive metamagnetic transition—unlike many of those previously studied by the magnetocaloric community—enables a broad range of magnetocaloric working temperatures around room temperature to be covered by a single material, whilst harnessing the first order nature of the transition.

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